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CYCLOPROPANATION USING RHODIUM(III)PORPHYRINS : LARGE CIS VS TRANS SELECTIVITY

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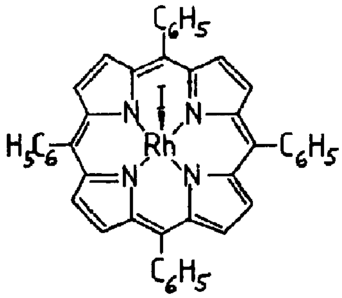
Abstract: Rhodium(III)tetraphenylporphyrin behaves as a sterically hindered cyclopropanation catalyst. Cis-cyclopropanes or "abnormal" products are obtained on reaction with cis-olefins or aromatics.

Cyclopropanation of cis-olefins using diazoesters + metal derivatives usually gives the trans cyclopropyl ester as the major product [1]. Rhodium(II)carboxylates are currently used for efficient cyclopropanation [2] but also show in some cases (especially Rh(II)pivalate) an increase of cis/trans ratio[2,3] (as was earlier noticed with copper-containing catalysts [4] but to a smaller extent).

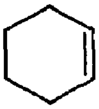
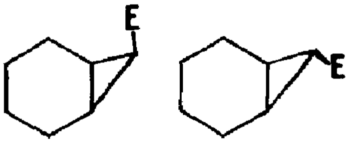
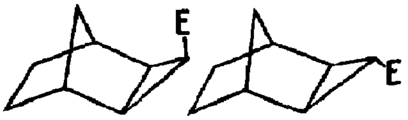
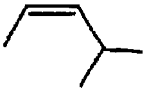
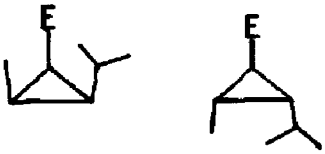
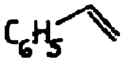
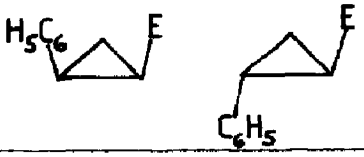
We wish to report that iodorhodium(III)mesotetraphenylporphyrin (RhTPPI) [5] not only is an efficient cyclopropanation catalyst [6] but also shows a remarkable cis selectivity.

The reactions were run at 60° in excess olefin using ethyldiazoacetate as reagent (olefin/diazoester ca 4 to 10; RhTPPI/diazoester ca 10^{-3} to 5×10^{-3}). The product were isolated using LC, HPLC and VPC. Yields correspond to isolated cyclopropanes and are not optimized. The collected N_2 volume reached ca 100 % in most cases.



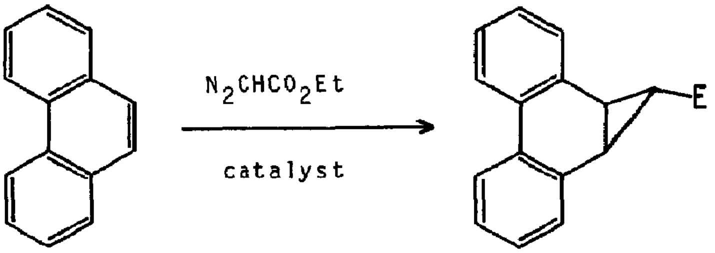
RhTPPI

For comparison reactions using Rh(II)pivalate (Rhpiv) [3] or CuCl were run under identical conditions (see Table).

olefin	products cis E = CO_2Et trans	catalyst	cis/trans ratio	total cyclopropane yield (RhTPPI)
	 	RhTPPI Rhpiv CuCl	<u>0.84</u> 0.32 (ref.3) 0.12 [a]	62 %
	 	RhTPPI Rhpiv CuCl	<u>1.85</u> 0.44 0.02 [b]	71 %
	 	RhTPPI Rhpiv CuCl	<u>4.9</u> 2.2 0.56	60 %
	 	RhTPPI Rhpiv	1.13 0.67 c	71 %

a) Maximum 0.26 using Moser's catalysts [4] (0.42 using Br_2CHCO_2R + Cu (ref. 8) ; 0.62 photochemically but yield is low and the insertion product present). b) 0.22 to 0.33 using CuCN (ref. 9). c) maximum 0.62 using Moser's catalysts [4] but 1.2-1.67 with Cobaltdioximes (ref. 10).

In order to test the reactivity of aromatic rings phenanthren was subjected to the same reaction conditions :

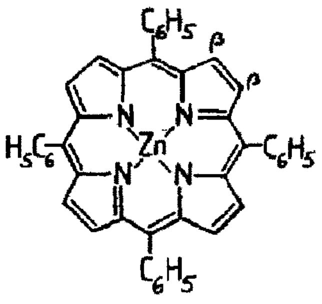


and other monoesters

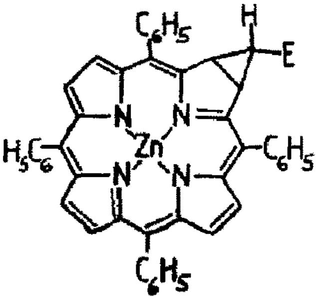
"trans"

Catalyst	total yield monoesters [11]	"trans"/total monoesters
CuCl	17 %	96 %
Rhpiv	38.5 %	21 %
RhTPPI	51 %	8.5 %

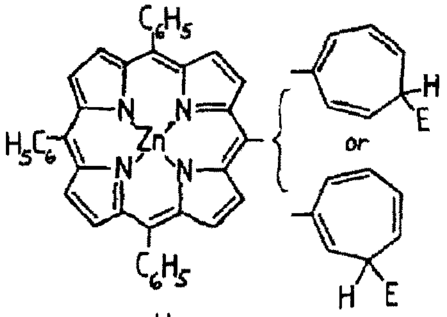
The most hindered cis double bond tested was the ββ double bond of ZnTPP. Copper catalysis gave the expected chlorins [12] (42 % / transformed starting material, cis/trans = 0.1) while RhTPPI gave homologation of one peripheral phenyl group (26 % H / transformed starting material ; trace of cis chlorin detected) [13].



ZnTPP



cis + trans chlorins



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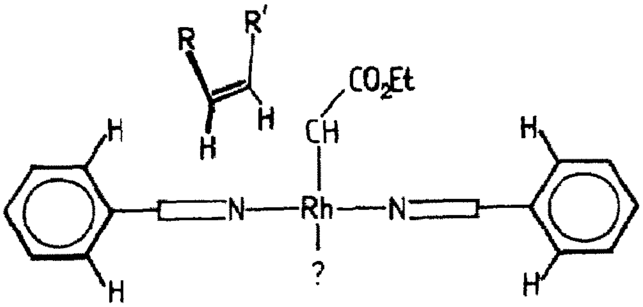
If one considers the formation of an intermediate rhodium-carbene complex [14] these results may be interpreted in terms of steric hindrance between the olefin substituents and the bulky porphyrin ligand (macrocycle + 4 statistically perpendicular phenyl groups).



side view of a possible intermediate
+ approaching olefin

An approach like that depicted above may be prefered since the double bond substituents are kept away from the porphyrin and will eventually give the cis-cyclopropane.

In the case of phenanthrene the "normal" product (trans-cyclopropylester) will decrease while isomers corresponding to more accessible positions (as well as the 9,10 cis-isomer) are favored.

The ZnTPP case is extreme since no approach of the pyrrolic ββ bond in the vicinity of the reactive center is possible (phenyl-phenyl + phenyl-macrocycle interactions). The only remaining possibility is the attack of the least hindered group, thus demonstrating that the notoriously inert phenyls of TPP's can be modified in the presence of reactive pyrrolic bonds.

REFERENCES

1. Review on diazoacetic esters cyclopropanation: V. Dave and E.W. Warnhoff, Organic Reactions, 18, 217 (1970). Example of more recent work : P.H. Mazzocchi and H.J. Tamburin, J. Org. Chem., 38, 2221 (1973).
2. A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot and P. Teyssié, J. Org. Chem., 45, 695 (1980) and earlier publications from the same group.
3. D. Holland and D.J. Milner, J. Chem. Res. (S), 317 (1979) ; J. Chem. Res. (M), 3734 (1979).
4. W.R. Moser, J. Amer. Chem. Soc., 91, 1135 (1971).
5. Prepared according to : H.J. Callot and E. Schaeffer, Nouv. J. Chim., 4, 311 (1980).
6. Insertion in OH bond of MeOH (53 %; ref. 5) and C-H bond of cyclohexane (65 %; unpublished) was also observed. More on this will be published elsewhere.
7. The reaction is slow at 20°C. The selectivity of the cyclohexene / ethyldiazoacetate reaction did not vary over the 20°-60°C range.
8. N. Kawabata, M. Naka and S. Yamashita, J. Amer. Chem. Soc., 98, 2676 (1976).
9. R.R. Sauers, S.B. Schlosberg and P.E. Pfeffer, J. Org. Chem., 33, 2175 (1968).
10. A. Nakamura *et al.*, J. Amer. Chem. Soc., 100, 3443, 3449 (1978).
11. The detailed composition of the reaction mixture will be published elsewhere.
12. H.J. Callot, Bull. Soc. Chim. Fr., 4387 (1972).
13. No reaction product (traces) observed with Rhpiv.
14. As usually postulated : see ref. 2, 3, 5.

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